A *grating* monochromator of BL23SU at SPring-8 covering silicon and oxygen *K*-edges

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We report the present performance of a *grating* monochromator at the newly constructed soft x-ray beamline (BL23SU at the SPring-8), which can measure both silicon and oxygen *K*-edges. That provides new opportunities for XAFS measurements of solids up to 2100 eV.

Keywords: x-ray absorption fine structure (XAFS), silicon and oxygen *K*-edges, soft x-ray beamline, varied-line-spacing plane *grating* (VLSPG) monochromator, BL23SU at SPring-8.

1. Introduction

X-ray absorption fine structure (XAFS) spectroscopy including x-ray absorption near edge fine structure (XANES) and extended x-ray absorption fine structure (EXAFS) has been widely used by many researchers to obtain the information on the electronic states and the short-range local atomic structures of materials (Stöhr, 1992; Koningsberger *et al.*, 1988).

Synchrotron radiation (SR) is a suitable light source for XAFS measurements because it covers wide x-ray energy regions and provides a high photon flux and a variety of polarization of x-rays. XAFS measurements over Si *K*-edge energy regions have been generally carried out at a crystal monochrometor in x-ray beamline (Kitajima, 1995; Paul *et al.*, 1995; Robinson *et al.*, 1995; Jones *et al.*, 1995; Dann *et al.*, 1998). The available x-ray energy is essentially limited: *c.f.* a minimum x-ray energy is down to 1800 eV using the InSb(111) crystals or 1000 eV with a pair of YB_{66} crystals (Wong *et al.*, 1995). The energy region of a crystal monochromator does not cover lower than 1000 eV regions. In spite of many interesting low Z elements have *K*-edge in soft x-ray regions below 2000 eV, such as an oxygen *K*-edge, this problem has disturbed XAFS measurements. By now, there are a few beamlines which cover up to ~ 2000 eV with the same monochromator system using either crystal or grating (Kitajima *et al.*, 1999; Robinson, 1997).

In the field of Si MOS devices, the SiO_2 thin films are important material, thus a great deal of studies have been done (Engel, 1993). Normally, the SiO_2 films have been studied by XAFS measurements with two separate monochromators: crystal monochrometor (Si *K*-edge) and grating monochromator (O *K*-edge). Thus, the same *grating* monochromator which is able to measure silicon and oxygen *K*-edges has a great advantage. If XAFS measurements up to 2000 eV are accepted at the same soft x-ray beamline, it can give capability to investigate many low *Z*-element materials and moreover transition metal systems (c.f. catalysis) by using XANES and EXAFS measurements. The beamline BL23SU has been designed for the energy range of 0.5~1.5 KeV, however, it has been realized that the wider energy range is available for XAFS measurements.

All experiments were carried out at a soft x-ray beamline, BL23SU, which is a newly constructed JAERI beamline at the SPring-8. The BL23SU consists of a varied-line-spacing plane *grating* (VLSPG) monochromator in the soft x-ray region (Saitoh *et al.*, 2000 ; Yokoya *et al.*, 1998). This beamline has end-stations for wide variety of scientific studies, such as surface chemistry (Teraoka *et al.*, 1999), radiation biological chemistry, a photoemission spectroscopy and a magnetic circular dichroism (Yokoya *et al.*, 1998; Nakatani *et al.*, 1998). An undulator (ID23), so called APPLE-2 (advanced planar-plorized light emitter), has been installed as a light source (Sasaki *et al.*, 1994).

In this paper, we report the present performance of XAFS measurements up to 2100 eV using a VLSPG monochromator at BL23SU in the SPring-8. We used silicon substrates to check the soft x-ray beamline performances referring the results obtained another x-ray beamlines (Nagashima *et al.*, 1993; Comin *et al.*, 1985; Kawai *et al.*, 1999; Li *et al.*, 1993; Tanaka *et al.*, 1995). New capabilities are also presented to study XAFS measurements for Si and O *K*-edges with high performances.

2. Experimental

We used 0°-off N-type Si(001) substrates with 0.02 Ω cm with thickness of 500 μm in this study. Silicon oxide thin films on silicon substrates were formed by following wet-chemical treatments. (1) Substrates are boiled in alcohol. (2) Native oxide layers were etched in HF: H_2O= 1: 50 solution for 3 min. (3) After this etching process, substrates were rinsed in de-ionized water for 10 min, (4) In order to form thin oxide layers, substrates were boiled in NH_4OH: H_2O_2: H_2O=1: 4: 20 solution at 60°C for 10 min. (5) Finally substrates were rised in deionized water for 10 min. The HF etched samples are prepared by the step (3) process. An SiO_2 powder sample, which was sticked to a sample holder with a conductive carbon tape, was measured as a standard sample.

XAFS spectra (I/I_0) were recorded as the total electron yield (TEY) at room temperature in the ultra-high vacuum condition, where I is sample current and I_0 is the mirror current to monitor the incident photon intensity. The incident angle of incoming x-rays was normal to the sample surface. At the oxygen *K*-edge, XAFS measurements are carried out using circular-polarized light. At the Si *K*-edge, the elliptically-polarized light was used to avoid the heat load of optical components. An x-ray energy was confirmed by Au4*f* binding energy by using an electron energy analyzer of the surface chemistry end-station. We used a groove density 600 *l/mm* grating and a groove density 1000 *l/mm* grating to measure the O *K*-edge and the Si *K*-edge spectra, respectively. These gratings can be changed in vacuum. The photon flux is estimated over 10^{11}photons/sec/0.02% b.w. which is normalized to a stored electron current of 100 mA (Saitoh *et al.*, 2000). The horizontal and the vertical full-width of half maximum of SR beams at the surface chemistry station are less than 2.0 and 1.0 mm, respectively (Yokoya *et al.*, 1998).

3. Results and discussion

Figure 1 shows XANES spectra of both (i) Si and (ii) O *K*-edges of silicon oxide thin films on Si(001) substrate formed by wet-chemical treatment (spectrum A) and a HF etched Si(001) substrate (spectrum B). In Fig. 1 (i), the XANES spectrum of the Si *K*-edge, the arrow **a** is assigned to the 1*s*→3*p* transition which indicates the density of the unoccupied conduction-band density of states (Nagashima *et al.,* 1993). It is noted that the double structure due to the spin-orbit splitting is clearly observed. The splitting width is smaller than 0.9 eV, thus the energy resolving power E/ΔE of the beamline was estimated better than 2000 (Yagi; Yang *et al.,* 1992). The arrow **b** was associated with Si(-O) 1s absorption of the surface oxide (Kasrai *et al.,* 1996). The present XANES spectra reproduce the previous results. It is realized that the *grating* monochromator is available for the energy region up to 2100 eV for the XANES of solids (Dann *et al.,* 1998; Kasrai *et al.,* 1996; Kitajima., 1995).

Referring the Si *K*-edge XANES reported by Kasrai *et al,* (1996), we estimate the thickness of silicon oxide layers formed by wet-chemical treatements to be smaller than 1.0 nm. The Si *K*-edge XANES results also indicate that the silicon oxide thin films formed by an wet-chemical treatment are similar to anodic silicon oxides (Kasrai *et al.,* 1996), not that of non-stoichiometric SiO_x films (Belot *et al.,* 1991).

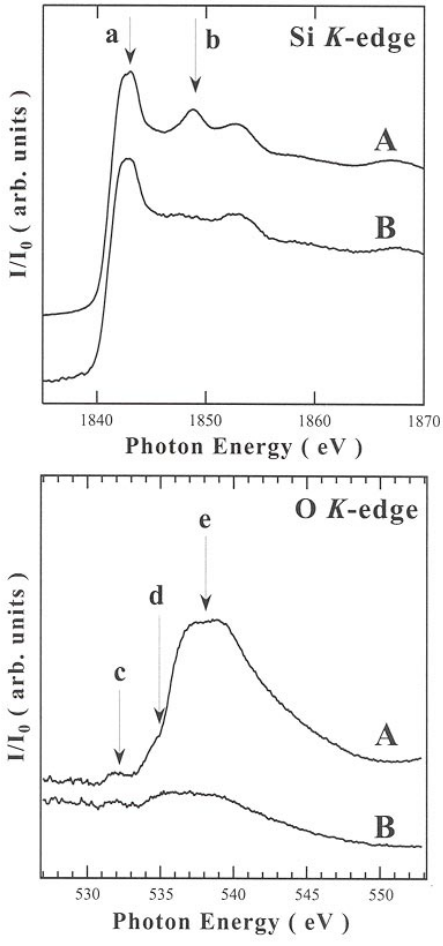

Figure 1
XANES spectra of (I) Si and (ii) O *K*-edges of a Si(001) substrate formed by A) wet-chemical treatment and B) a HF etched Si(001) substrate.

Figure 1(ii) shows XANES spectra at the O *K*-edge of silicon oxide thin films. The O2*p* conduction band structures are well resolved, which are indicated by the arrows **c**, **d** and **e** in spectrum A. We assigned the arrow **c** to 1*s*→O2*p*(-Si3*s*), the arrow **d** to 1s→O2*p*(-Si3*p*), and the arrow **e** to O2*p*(-Si3*s*) and O2*p*(-Si3*p*) transitions (Tanaka *et al*., 1995). This result also shows that BL23SU provides XAFS measurements at O *K*-edge with high energy resolutions (Saitoh *et al.,* 2000). The HF treated Si(001) substrate (spectrum B in Fig. 1 (ii)) does not have thick silicon oxide films, so that the O2*p* conduction band structure is not clearly observed.

Figure 2 shows Si *K*-edge spectra (EXAFS regions) of a Si(001) substrate formed by a wet-chemical treatment and a SiO_2 powder sample. The observed spectra seems to be quite similar to that of the amorphous SiO_2 obtained by the transmission method (Nagashima *et al.,* 1993; Kitajima., 1995). The difference between spectra A and B in Fig. 2 is due to the overlap of Si substrate absorption background. In order to subtract the substrate absorption, it is necessary to use more surface sensitive XAFS methods, such as a partial electron yield (PEY) method.

The EXAFS oscillations have been observed in the spectrum over 1860 eV. In order to show an advantage of the beamline more clearly, we analyzed the EXAFS spectrum (spectrum A in Fig. 2) from the point of view of the EXAFS oscillations and its Fourier transform. Figures 3 (i) and (ii) show EXAFS oscillation function and its Fourier transformation, respectively. Comparing EXAFS spectrum of a Si(001) surface reported by Kitajima, (1995) we assign the strong peak at 2.0 Å shown in Fig. 3 (ii) to the Si-Si bonding without the correction of phase shifts caused by photoelectrons scattered by neighbor atoms. The result obtained by the *grating* monochromator also demonstrates the availability for the EXAFS measurements of solids under 2100 eV region.

The peak corresponding to the Si-O bonding at 1.25 Å (Kitajima., 1995) was not observed in our EXAFS spectrum, since the amount of SiO_2 films is small and the signal of SiO_2 is hidden in the signal of substrate Si atoms in the TEY measurement. Moreover, since the photon energy range was limited up to 2050 eV corresponding to 7.4 $Å^{-1}$ in this study, it is not able to resolve the short distance regions. For the latter problem, it is necessary to make the control

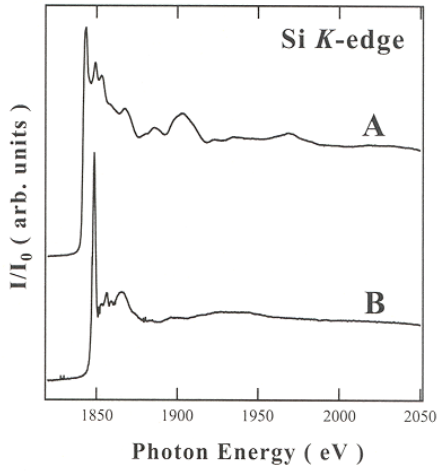

Figure 2
Si *K*-edge EXAFS spectra of A) a Si(001) substrate formed by wet-chemical treatment and B) the SiO_2.powder sample.

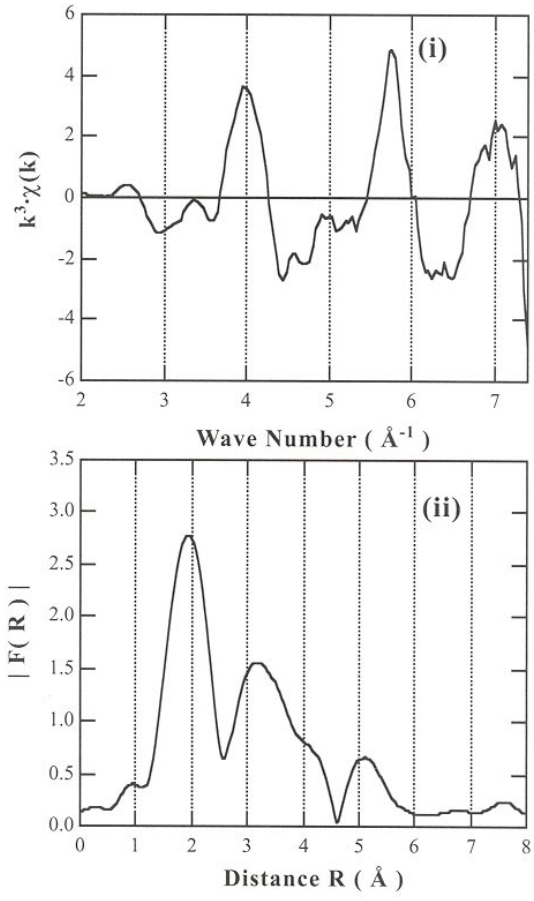

Figure 3
(i) Oscillation function and (ii) its Fourier transform of a Si(001) substrate formed by wet-chemical treatment.

systems simultaneously driving the monochromator and the ID23 during XAFS measurements. We also have a plan to study in detail the nature of silicon oxide thin film formed by wet chemical treatments to the future.

4. Summary

We report the present performance of the newly constructed soft x-ray beamline (BL23SU) up to 2100 eV, which consists of a VLSPG monochromator at the SPring-8. We have measured both Si and O *K*-edges XAFS measurements on a chemical treated Si(001) substrate at the same beamline. The silicon oxide films formed on the Si(001) substrate by the wet chemical treatment are ascribed to amorphous SiO_2 rather than non-stoichiometric SiO_x films. The *grating* monochromator beamline, BL23SU, covers up to 2100 eV in the soft x-ray region. Although the Si and O *K*-edges XAFS are normally studied at separate beamlines, it is possible to perform these *K*-edge XAFS measurements at the same beamline with BL23SU at SPring-8. We confirmed that it proved great opportunities to study of soft x-ray spectroscopy.

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